SUPERCONDUCTIVITY

1. Introduction

With his experiments on liquid helium in 1908, Kamerlingh Onnes marked the beginning of the history of superconductivity. In fact, in 1911 he observed a brutal fall of the electrical resistance of mercury, when the temperature went below the critical temperature of 4.19 K.

Resistance of mercury at low temperatures

He named this particular state “superconductivity”. He observed, moreover, that the superconductivity disappeared above a critical current \( j_c \), or under the application of a magnetic field \( H_c \).

A superconductor is an ideal diamagnetic, i.e., the magnetic induction \( B \) vanishes inside a superconductor. This effect, which was discovered by Meissner and Ochsenfeld, is known by the name of “Meissner effect” (1933). Several years have past before the physicists could provide a coherent explanation to the phenomenon of superconductivity. One tried first to study the phenomenon with the help of macroscopic theories, such as thermodynamics and electrodynamics. In 1934, Gorter and
Casimir developed a first thermodynamical theory of superconductivity. In 1935, London studied its electrodynamics and explained the Meissner effect.

The most complete phenomenological theory was elaborated in 1950 by Ginzburg and Landau. This theory uses the gauge invariance and introduces a non measurable quantity called the “order parameter”. It allows to understand the superconductivity phenomenon around the critical temperature. It has led Abrikosov (1957) to the hypothesis of a vortex lattice, which appears in the material in the presence of a magnetic field and which has been confirmed experimentally ten years later.

The path towards the microscopic theory of superconductivity was also very long. The experimental observations, which have led to the success of the microscopic theory are essentially:
- an energy gap in the electronic spectrum
- the isotope effect.

The direct observation of an energy gap (forbidden band) was made thanks to experiments using the tunnel effect (1960). By isotope effect one means the dependence of the critical temperature on the mass $M$ of the atom:

$$T_c \sim M^{-\alpha}, \quad \alpha \approx 0.5$$

Nevertheless, this behavior is not the same for all the materials, as you can see in the table below:

<table>
<thead>
<tr>
<th></th>
<th>$\alpha$</th>
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<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Hg$</td>
<td>$0.50 \pm 0.03$</td>
<td>$Cd$</td>
<td>$0.50 \pm 0.10$</td>
</tr>
<tr>
<td>$Tl$</td>
<td>$0.50 \pm 0.10$</td>
<td>$Mo$</td>
<td>$0.33 \pm 0.05$</td>
</tr>
<tr>
<td>$Sn$</td>
<td>$0.47 \pm 0.02$</td>
<td>$Ru$</td>
<td>$0.00 \pm 0.10$</td>
</tr>
<tr>
<td>$Pb$</td>
<td>$0.48 \pm 0.01$</td>
<td>$Os$</td>
<td>$0.20 \pm 0.05$</td>
</tr>
</tbody>
</table>

The isotope effect allowed Fröhlich in 1950 to propose the electron-phonon interaction as responsible for the superconductivity. We needed however, to wait until 1957 to see Bardeen, Cooper and Schrieffer use this hypothesis in order to describe quantitatively the superconductivity in terms of electron pairs (Cooper pairs) bound by a weak attraction. This is the “BCS theory”.

During the sixties and seventies, new superconducting materials have been discovered: Bechgaard salts and heavy fermions. The microscopic theory of this superconductors is not yet completely clarified. The development of the superconductivity stagnated a bit during these years. One thought to find a situation of saturation around $T_c \sim 23$ K. In 1986, Georg Bednorz and Alex Müller, with their experiments on $La_{2-x}Ba_xCuO_4$ modified in a complete manner the data about superconductivity. These materials are doped insulators ($La_{2}CuO_4$ is a Mott insulator), with a very anisotropic structure, in layers, where $CuO_2$ planes alternate with charge reservoirs ($La$, $Ba$, etc...). By modifying the components between the planes, other ceramics have been discovered, such as $YBa_{2}Cu_{3}O_{7-\delta}$, $Bi_2Sr_2CaCu_2O_{8+\delta}$, etc... In a short time, materials with $T_c$ as high as $\sim 130$ K have been discovered. Recently, superconductivity has been also found in simpler materials, such as $MgB_2$ (this one has been discovered very recently). However, for the moment the critical temperature remains still very modest, i.e., around $T_c \sim 50$ K.
In this course, we will first discuss the macroscopic theories, such as the London theory and the Ginzburg-Landau theory. Then we will go to the microscopic BCS theory. At the end, I will try to give you a general idea about high-$T_c$ superconductors. Unfortunately, we will not have time, neither to discuss the origin of the attractive interaction (electron-phonon), nor to develop more elaborated theories, such as Eliashberg theory.

Evolution of the critical temperature $T_c$
2. London theory

Before providing a theoretical description of superconductivity, we have to review the main thermodynamical and electromagnetic properties of superconductors and define the physical framework in which they will be analyzed.

A very large class of materials has the property of completely losing their electrical resistivity below a critical temperature $T_c$. This phase transition is attributed to an electronic property of the material. Besides the zero resistivity, superconductors exhibit the Meissner effect: if one applies a magnetic induction $B$ to a cool superconductor, below $T_c$ we find $B = 0$ inside the sample. In addition, the Meissner effect indicates that a magnetic field $B$ applied to a superconducting material in the normal phase, is expelled to outside the material when one goes below $T_c$.

![Diagram showing Meissner effect](image)

$T > T_c$ \hspace{1cm} $T < T_c$

The Meissner effect occurs for low magnetic fields. Experiments show that there is a critical field $H_c(T)$ above which the sample becomes normal again. For the pure superconductors, we have the formula

$$H_c(T) = H_c(0) \left[1 - \left(\frac{T}{T_c}\right)^2\right]$$

The critical field $H_c(T)$ has the following behavior:

![Critical field behavior](image)
Besides this magnetic properties, the superconductors have thermodynamical properties. At zero magnetic field, the transition between the normal and the superconducting state is of second order, what implies a discontinuity in the specific heat \( c \):

\[
C
\]

\[
C_n
\]

\[
C_s
\]

\[
T_c
\]

\[
T
\]

2.1. Thermodynamical relations

The superconductivity represents a thermodynamical system in equilibrium (during the observation, the system appears to be independent of time, history, and there is no flux of matter or energy). The superconductor is in fact characterized by the condition \( \mathbf{B} = 0 \), independently of the way this state is reached. We can therefore apply the thermodynamic techniques to treat it. The Helmholtz free energy density is

\[
df = -SdT + \frac{1}{4\pi} \mathbf{H} \cdot d\mathbf{B}
\]

where the second term represents the energy due to the magnetic work.

We have therefore

\[
\left( \frac{\partial f}{\partial \mathbf{B}} \right)_T = \frac{1}{4\pi} \mathbf{H}.
\]

The magnetic induction \( \mathbf{B} \) is not directly measurable. By performing a Legendre transformation, one may obtain the Gibbs free energy density \([f \to g; \ \mathbf{B} \to \mathbf{H}]\)

\[
g(T, \mathbf{H}) := f(T, \mathbf{B}) - \frac{1}{4\pi} \mathbf{B} \cdot \mathbf{H}
\]

\[
dg = -SdT - \frac{1}{4\pi} \mathbf{B} \cdot d\mathbf{H}.
\]

(2)

We obtain from this

\[
\left( \frac{\partial g}{\partial \mathbf{H}} \right)_T = -\frac{1}{4\pi} \mathbf{B}
\]

(3)
Consider a long superconducting cylinder in a magnetic field \( \mathbf{H} = \mathbf{H}_e \). Therefore, at constant temperature, equation (3) gives

\[
g(T, \mathbf{H}) - g(T, 0) = -\frac{1}{4\pi} \int_0^{\mathbf{H}} \mathbf{B}(\mathbf{H}') d\mathbf{H}'
\]

In the normal state, the majority of superconductors are non-magnetic, i.e., \( \mathbf{H} = \mathbf{B} \) [\( \mathbf{H} = \mathbf{B} - 4\pi \mathbf{M} \)]. Therefore,

\[
g_n(T, \mathbf{H}) - g_n(T, 0) = -\frac{1}{8\pi} \mathbf{H}^2.
\] (4)

In the superconducting state \( \mathbf{B} = 0 \) and thus

\[
g_s(T, \mathbf{H}) = g_s(T, 0).
\] (5)

On the other hand, at the critical field \( \mathbf{H}_c \) the two phases are in thermodynamical equilibrium,

\[
g_s(T, \mathbf{H}_c) = g_n(T, \mathbf{H}_c).
\] (6)

By combining these 3 last equations, we find

\[
g_s(T, 0) = g_s(T, \mathbf{H}_c) = g_n(T, 0) - \frac{1}{8\pi} \mathbf{H}_c^2
\]

and hence

\[
f_s(T, 0) = f_s(T, \mathbf{H}_c) = f_n(T, 0) - \frac{1}{8\pi} \mathbf{H}_c^2.
\] (7)

We also find the result

\[
g_s(T, \mathbf{H}) - g_n(T, \mathbf{H}) = g_s(T, 0) - g_n(T, \mathbf{H}) = \frac{1}{4\pi} \left( \mathbf{H}^2 - \mathbf{H}_c^2 \right)
\]

which proves that the superconducting phase is the equilibrium state for all \( \mathbf{H} < \mathbf{H}_c \). In fact, one may show in thermodynamics that for a system at constant temperature and pressure, the Gibbs potential never increases, or more precisely, the equilibrium state is the state with minimum Gibbs potential. By taking the derivative of the Gibbs potential, we obtain the entropy difference \( S = -\partial g/\partial T \) between the two phases

\[
S_s(T, \mathbf{H}) - S_n(T, \mathbf{H}) = \frac{1}{4\pi} \mathbf{H}_c \frac{d\mathbf{H}_c}{dT}
\] (8)

The curve \( \mathbf{H}_c(T) \) shows that \( d\mathbf{H}_c/dT < 0 \), what proves that the superconducting phase has a lower entropy than the normal phase. Moreover, the specific heat

\[
c_H = T \left( \frac{\partial S}{\partial T} \right)_{\mathbf{H}}
\]

provides the difference

\[
c_{s\mathbf{H}} - c_{n\mathbf{H}} = \frac{T}{4\pi} \left[ \left( \frac{d\mathbf{H}_c}{dT} \right)^2 + \mathbf{H}_c \frac{d^2\mathbf{H}_c}{dT^2} \right]
\]
which, at the critical temperature \([H_c(T_c) = 0]\), provides the jump of the specific heat (see figure)

\[
(c_s - c_n)_{H_c} = \frac{T_c}{4\pi} \left( \frac{dH_c}{dT} \right)_{T_c}^2.
\]

The behavior of \(H_c(T)\) for \(T \to 0\) is in agreement with the 3rd thermodynamical law, because the difference (8) gives for \(S_s \to 0, \ S_n \to 0, \ dH_c/dT \to 0\).

2.2. The electrodynamics of superconductivity

The London theory is primarily based on the electro-dynamical properties of a superconductor. Suppose that all the electrons in the material are superconducting. If one applies an electric field \(\mathbf{E}\) to the sample, the superconducting electrons will be accelerated without dissipation. This allows one to write the Newton’s equation

\[
m \frac{dv_s}{dt} = -e\mathbf{E}
\]

and the super-current

\[
\mathbf{j}_s = -en_s \mathbf{v}_s
\]

from which

\[
\frac{d\mathbf{j}_s}{dt} = \frac{e^2n_s}{m} \mathbf{E}.
\]

Then, the induction law of Faraday

\[
\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t}
\]

provides the equation

\[
\frac{d}{dt} \left( \nabla \times \mathbf{j}_s + \frac{e^2n_s}{mc} \mathbf{B} \right) = 0.
\]

We can now use Ampere’s law

\[
\nabla \times \mathbf{B} = \frac{4\pi}{c} \mathbf{j}_s + \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t}
\]

and suppose that the time variation of the field \(\mathbf{E}\) is weak, in a way that the displacement current \(\frac{1}{c} \frac{\partial \mathbf{E}}{\partial t}\) = 0. Therefore with the identity

\[
\nabla \times (\nabla \times \mathbf{B}) = \nabla (\nabla \cdot \mathbf{B}) - \nabla^2 \mathbf{B} = \frac{4\pi}{c} \nabla \times \mathbf{j}_s
\]

we obtain, with the condition \(\nabla \cdot \mathbf{B} = 0\), the equation

\[
\frac{d}{dt} \left( \nabla^2 \mathbf{B} - \frac{4\pi e^2n_s}{mc^2} \mathbf{B} \right) = 0
\]

We define the “London penetration depth”

\[
\lambda_L^2 := \frac{mc^2}{4\pi n_sc^2}
\]
With a hypothesis stronger than \((..) = \text{const.}\) with time, London postulated the equation

\[
\nabla^2 \mathbf{B} - \frac{1}{\lambda_L^2} \mathbf{B} = 0
\]

London equation above may also be deduced by minimizing the total energy

\[
E := \frac{1}{2} \int d^3 r \left[ \frac{\mathbf{B}^2}{4\pi} + n_s m \mathbf{v}_s^2 \right] = \frac{1}{2} \int d^3 r \left[ \frac{\mathbf{B}^2}{4\pi} + \frac{m}{n_s e^2} \mathbf{j}_s^2 \right]
\]

(10)

The permanent current is coupled to the magnetic induction by the Ampere’s law,

\[
\nabla \times \mathbf{B} = \frac{4\pi}{c} \mathbf{j}_s,
\]

from which we obtain the energy

\[
E = \frac{1}{8\pi} \int d^3 r [\mathbf{B}^2 + \lambda_L^2 (\nabla \times \mathbf{B})^2].
\]

Minimization of the functional \(E(\mathbf{B})\) gives

\[
\mathbf{B} + \lambda_L^2 \nabla \times (\nabla \times \mathbf{B}) = 0
\]

and provides, with the condition \(\nabla \cdot \mathbf{B} = 0\), the London equation

\[
\nabla^2 \mathbf{B} - \frac{1}{\lambda_L^2} \mathbf{B} = 0.
\]

In a superconducting sample, the magnetic induction \(\mathbf{B}\) behaves as

\[
\mathbf{B}(z) = (B_x(0), 0, 0)e^{-z/\lambda_L}
\]

\[\text{vide supra}\]
There are similar equations for \( \mathbf{j} \) and \( \mathbf{E} \) with the conditions \( \nabla \cdot \mathbf{j} = 0 \) and \( \rho = 0 \) (charge neutrality in a superconductor). In a bulk with dimension \( \sim \lambda_L \), susceptibility measurements allow to determine \( \lambda_L \):

\[
\mathbf{B} = \mathbf{H} + 4\pi \mathbf{M} = \mathbf{H}(1 + 4\pi \chi).
\]

2.3. Coherence length

Besides the London penetration depth \( \lambda_L \) (9), there is another characteristic length for superconductivity: it is the coherence length \( \xi \). In the microscopic theory, one may show that it describes the domain where the velocity of two electron is correlated. One may evaluate this length with the help of the gap energy \( 2\Delta \), which one finds experimentally in superconductors during tunneling experiments. The energy gap \( 2\Delta \) is centered at the Fermi energy. We have therefore

\[
\Delta = \delta \left( \frac{p^2}{2m} \right) = \frac{p_F}{m} \delta p = \hbar v_F \delta k.
\]

One defines the “coherence length”

\[
\xi :\sim \frac{1}{\delta k} = \frac{\hbar v_F}{\Delta}.
\]

It represents the characteristic length of spatial fluctuations in the superconductor. We have therefore a length scale which provides a validity criterion for the London theory, where the values of \( \mathbf{B} \) and \( \mathbf{j} \) vary very slowly,

\[
\lambda_L \gg \xi.
\]

In a normal metal, the plasma frequency is

\[
\omega_p = \left( \frac{4\pi n e^2}{m} \right)^{1/2} \sim 10^{16} \text{s}^{-1}
\]

in a way that

\[
\lambda_L = \frac{c}{\omega_p} \sim 300 \text{Å}.
\]

In a superconductor, the gap energy is \( \Delta \approx 1 \text{ meV} \) and the Fermi energy \( E_F \approx 5 \text{ eV} \). Therefore, with \( k_F \approx 1 \text{Å}^{-1} \) we obtain

\[
\xi = \frac{2E_F}{k_F \Delta} \approx 2 \cdot 10^4 \text{Å}.
\]

We notice here that the validity criterion of the London theory is not satisfied for the normal metals. In the case when \( \lambda_L \ll \xi \), we talk about type I superconductor.

The alloys and high-\( T_c \) superconductors have electrons with an effective mass much larger, and consequently a penetration depth longer than \( \lambda_L \sim 1000 \text{Å} \). On
the other hand, their transition temperature is higher, what gives a shorter coherence length \(2\Delta(0) \sim k_B T_c\): \(\xi \sim 10 - 100\,\text{Å}\). We are in the situation where 

\[\xi \ll \lambda_i.\]

These are type II superconductors. They have two critical fields \(H_{c1}\) and \(H_{c2}\). The Meissner effect is total only for weak fields, \(H < H_{c1}\). For fields \(H_{c1} < H < H_{c2}\) the material remains superconductor, but the magnetic flux partially penetrates the material. Above \(H_{c2}\) we find again the normal phase. The phase between \(H_{c1}\) and \(H_{c2}\) is called vortex phase or Shubnikov phase. The magnetization is continuous, i.e., there is a second order phase transition (no latent heat). The two diagrams below show a schematic representation of these phenomena.

\[\text{In the mixed state, between } H_{c1} \text{ and } H_{c2}, \text{ the flux of the field } B \text{ does not penetrate the material in a laminar way, but as a lattice of flux tubes, each one carrying a flux quantum } \Phi_0 = \hbar c/2e. \text{ It remains now to interpret the phenomenon of partial penetration of the magnetic flux. We have to distinguish essentially between the type I and type II superconductors. Consider both of them schematically,}\]

\[\text{In the gray zones, the superconductivity is strongly attenuated. The analysis of the vortex phase will be made in a more complete manner in the framework of the Ginzburg-Landau theory. We will study a flux line, by calculating, for instance, its energy per unit length, as well as the critical fields } H_{c1} \text{ and } H_{c2}. \text{ However, it is also}\]
important to admit that reality gets more complicated as one increases the magnetic field. The number of flux lines increases. The lines interact among themselves and form a lattice. This phenomenon, proposed by Abrikosov in 1957, was observed for the first time in type II superconductors in 1967, by means of decoration technique and later by neutron scattering. The measurement of the critical field allows to estimate the fundamental quantities \( \xi \) and \( \lambda \).
3. Ginzburg-Landau theory

London theory provides a first approach to superconductivity. As we have seen, it doesn’t provide a satisfying macroscopic description of all the superconductivity phenomena in the presence of an electromagnetic field. It doesn’t allow to consider simultaneously both phases: the sample is either completely superconducting or completely normal.

3.1. The Landau free energy

The understanding of the thermodynamics of superconductivity started in 1934, when Gorter and Casimir introduced the concept of order parameter \( \psi \), where \(|\psi|^2\) is proportional to the density \( n_s \) of superconducting electrons. They postulated that near the transition temperature \( T_c \), the free energy is given by

\[
F = F_0 + V \left[ \alpha(T)|\psi|^2 + \frac{1}{2} \beta(T)|\psi|^4 \right]
\]

with the condition that \( \psi = 0 \) for \( T > T_c \). Around the phase transition, for \( (T - T_c) \ll 1 \) one may suppose that

\[
\alpha(T) = \alpha'(T - T_c) \quad \alpha' > 0
\]

\[
\beta(T) \approx \beta(T_c) > 0.
\]

By minimizing the free energy (11) we find

\[
\alpha'(T - T_c)\psi + \beta|\psi|^2\psi = 0
\]

whose solutions are

\[
\psi = 0 \quad \text{for} \quad T > T_c
\]

\[
|\psi| = \left( \frac{\alpha'}{\beta} \right)^{1/2} (T_c - T)^{1/2} \quad \text{for} \quad T < T_c.
\]

If one wants to take spatial fluctuations into account, one must consider an order parameter \( \psi(\mathbf{r}, t) \). Therefore, the Landau free energy is given by

\[
F = F_0 + \int d^3r \left[ \alpha(T)|\psi|^2 + \frac{\beta}{2} |\psi|^4 + \gamma |\nabla \psi|^2 \right]
\]

where the factor \( \gamma \) may be chosen equal to one by renormalization of \( \psi \). As Landau has noticed, the mean field behavior of the system in the neighborhood of the transition is completely determined by the expansion of the free energy (12). Because the order parameter vanishes at \( T_c \), higher order terms in the expansion are not important. We can visualize it in the following way, with the free energy density \( f \),

\[
f \sim \alpha|\psi|^2 + \beta|\psi|^4 + |\psi|^6 + \ldots
\]

\[
= \frac{\alpha^2}{\beta} \left[ \frac{\beta}{\alpha^2} |\psi|^2 + \frac{\beta^2}{\alpha^2} |\psi|^4 + \frac{\beta}{\alpha^2} |\psi|^6 + \ldots \right]
\]

\[
= \frac{\alpha^2}{\beta} \left[ \tilde{\psi}^2 + \tilde{\psi}^4 + \frac{\alpha}{\beta^2} |\tilde{\psi}|^6 + \ldots \right]
\]
where we noticed that $|\tilde{\psi}|^2 = (\beta/\alpha)|\psi|^2$. Thus, if $|\tilde{\psi}| \sim 1$, we have

$$|\tilde{\psi}|^4 \left(1 + \frac{\alpha}{\beta^2} |\tilde{\psi}|^2 + \ldots\right) \rightarrow |\psi|^4$$

when $T \rightarrow T_c$, because $\alpha \sim (T - T_c)$. We may conclude that for any free energy expressed in terms of the order parameter $\psi$, the critical behavior of the system may be studied by an expansion in powers of $|\psi|^2$ until the term $|\psi|^4$. Such an expansion is called Landau free energy. Well below $T_c$, the Landau expansion is no longer valid. The order parameter is then controlled by a complicated potential. The amplitude fluctuations of the order parameter become negligible in comparison with the phase fluctuations.

### 3.2. Ginzburg-Landau equations

The generalization of the Landau energy to an energy which contains the electromagnetic field is made by coupling the field $\mathbf{A}$ in a gauge invariant way. One applies simply the gauge principle:

$$F_s = F_n + \int_V d^3r \left[ \alpha |\psi|^2 + \frac{\beta}{2} |\psi|^4 + \frac{1}{2m^*} \left( \frac{\hbar}{i} - \frac{e^*}{c} \mathbf{A} \right) \psi \right]^2 + \frac{1}{8\pi} (\nabla \times \mathbf{A})^2 \right]$$

(13)

where $m^*$ is a free constant, as long as $\psi$ is not fixed. The parameter $e^*$ is not the electron charge. However, it was very early noticed that a good agreement with experiments was possible if $e^* \sim 2e$. We define as before

$$\alpha = \alpha'(T - T_c), \quad \alpha' > 0.$$  

Among all the parameters, $T_c, \alpha', \beta, m^*, e^*$ we will see that only one plays a non-trivial role: the Ginzburg-Landau parameter, defined as the ratio between the penetration depth $\lambda$ and the coherence length $\xi$ (see below).

When we consider the magnetic field $\mathbf{H}$, the essential thermodynamical quantity is the Gibbs potential, defined by (2). For an external uniform magnetic field $\mathbf{H}$

$$G_s(T, \mathbf{H}) = F_s(T, \mathbf{B}) - \frac{1}{4\pi} \int_V d^3r \mathbf{B} \cdot \mathbf{H}$$

où $\mathbf{B} = \nabla \times \mathbf{A}$. The equilibrium condition implies that $G_s$ be stationary under variation of $\psi^*$ and $\mathbf{A}$ under the constraint $\mathbf{B} = \nabla \times \mathbf{A}$. Minimization of the functional $G_s$ provides the Ginzburg-Landau equations (exercise):

$$\frac{1}{2m^*} \left( \frac{\hbar}{i} - \frac{e^*}{c} \mathbf{A} \right) \psi + \alpha \psi + \beta |\psi|^2 \psi = 0$$

$$\frac{c}{4\pi} \nabla \times \mathbf{B} = \frac{e^* \hbar}{2m^*} (\psi^* \nabla \psi - \psi \nabla \psi^*) - \frac{e^2}{m^* c} |\psi|^2 \mathbf{A}$$

(14)
where the surface integrals vanished with the help of the boundary conditions $\partial V$ of $A$ and $\psi$

$$n \cdot \left( \frac{\hbar}{i} \nabla - \frac{e^*}{c} A \right) \psi = 0$$

$$n \times (B - H) = 0.$$  \hspace{1cm} (15)

The first condition corresponds to $j_n|_{\partial V} = 0$ and the second to the continuity of the field tangent to the surface $\partial V$. The first equation (14) is a non-linear Schrödinger equation. The second equation (14) introduces the super-current

$$j := \frac{e^* \hbar}{2m^* i} (\psi^* \nabla \psi - \psi \nabla \psi^*) - \frac{e^*}{m^* c} |\psi|^2 A.$$  \hspace{1cm} (16)

Notice that the obtained equations are self-consistent: $\psi$ depends on $B$, $B$ is given by $j$, which on its turn depends on $\psi$. The order parameter $\psi$ is usually normalized with the help of the local electronic density

$$|\psi|^2 = n_s^* (\vec{r}).$$

There is no general solution for the Ginzburg-Landau equations. We will however provide a detailed analysis of some particular solutions, by distinguishing some extreme cases. Before that, it is useful to rewrite these equations in dimensionless unities. In order to do that, let us first determine which are the characteristic parameters of the model.

In the case of a uniform superconducting sample with $A = 0$ we have the solution $\psi = 0$. This is the normal state. We also have the solution

$$|\psi|^2 = -\frac{\alpha}{\beta}, \quad \frac{\alpha}{\beta} < 0, \quad \frac{|\alpha|}{\beta} =: n_s^*.$$

This is the superconducting state, with $F_s(T,0) = F_n(T,0) - \alpha^2/2\beta$ (13). Because $F_s(T,0) = F_n(T,0) - H_s^2/8\pi$ (7), we have

$$\frac{\alpha^2}{\beta} = \frac{H_s^2}{4\pi},$$  \hspace{1cm} (17)

i.e., $\beta > 0$ and $F_s$ bounded by below.

Another simple case:

$A = 0$ and $\psi(z)$, allows us to introduce the coherence length $\xi$ and to get a first idea of the order parameter. In this case, the Ginzburg-Landau equation becomes

$$-\frac{\hbar^2}{2m^*} \frac{d^2 \psi}{dz^2} + \alpha \psi + \beta |\psi|^2 \psi = 0.$$

Suppose that $\psi(z)$ is real. With $\psi_\infty = \sqrt{\alpha/\beta}$, one may define the dimensionless order parameter

$$f(z) = \psi(z)/\psi_\infty.$$
We obtain then the equation
\[- \frac{\hbar^2}{2m^*|\alpha|} f''(z) - f(z) + f^3(z) = 0\]
which defines in a natural way the Ginzburg-Landau coherence length
\[\xi^2(T) := \frac{\hbar^2}{2m^*|\alpha|} = \frac{\hbar^2}{2m^*(T_c - T)\alpha'}\]
with the property \(\xi(T) \to \infty\) for \(T \to T_c\). This length is the characteristic scale of the variation of the order parameter \(\psi\). It is an important parameter in superconductivity, as well as the penetration depth
\[\lambda^2 := \frac{m^*c^2}{4\pi e^* n^*_s}\]
which characterizes the spatial variation of the magnetic induction.

It is now missing to solve the equation
\[-\xi^2 f'' - f + f^3 = 0\]  \hspace{1cm} (18)
subject to the boundary conditions \(f(0) = 0, f(\infty) = 1\). By multiplying (18) by \(f'\), we find
\[-\xi^2 f' f'' - f' f + f' f^3 = 0\]
\[- \frac{\xi^2}{2} (f'^2)' - \frac{1}{2} (f^2)' + \frac{1}{4} (f^4)' = 0\]
\[-\xi^2 f'^2 - f'^2 + \frac{1}{2} f^4 = c\]  \hspace{1cm} (19)
where the integration constant \(c = -1/2\) is fixed by the condition \(f'(\infty) = 0\). Thus the equation
\[\xi^2 f'^2 = \frac{1}{2} (1 - f^2)^2\]
whose solution obeying \(f(0) = 0, f(\infty) = 1\) is
\[f(z) = \tanh \left( \frac{z}{\sqrt{2}\xi} \right). \hspace{1cm} (20)\]

The characteristic lengths appearing in the Ginzburg-Landau theory are the coherence length \(\xi\)
\[\xi^2(T) = \frac{\hbar^2}{2m^*|\alpha|}\]  \hspace{1cm} (21)
and the penetration depth \(\lambda\)
\[\lambda^2 := \frac{m^*c^2}{4\pi e^* n^*_s}\]  \hspace{1cm} (22)
where the super-electron density is given by

\[ n^*_s = |\psi_\infty|^2 = \frac{|\alpha|}{\beta}. \]

In addition we have (17)

\[ H_c^2 = 4\pi \frac{\alpha^2}{\beta}. \]

We define the dimensionless quantity called the Ginzburg parameter

\[ \kappa := \frac{\lambda}{\xi} \frac{m^*c}{\hbar e^*} \left( \frac{\beta}{2\pi} \right)^{1/2} = \frac{\sqrt{2}e^*}{\hbar c} H_c \lambda^2. \quad (23) \]

Therefore, the following dimensionless quantities

\[ \tilde{r} = r/\lambda \quad \tilde{\psi} = \psi/|\psi_\infty| \]
\[ \tilde{B} = B/\sqrt{2}H_c \quad \tilde{A} = A/\sqrt{2}H_c \lambda \quad (24) \]

allow to rewrite the Ginzburg-Landau equations (14) as

\[ -\left( \frac{1}{i\kappa} \tilde{\nabla} - \tilde{A} \right)^2 \tilde{\psi} + \tilde{\psi} - |\tilde{\psi}|^2 \tilde{\psi} = 0 \]
\[ \tilde{\nabla} \times \tilde{B} = \frac{1}{2i\kappa} \left( \tilde{\psi}^* \tilde{\nabla} \tilde{\psi} - \tilde{\psi} \tilde{\nabla} \tilde{\psi}^* \right) - \tilde{A} |\tilde{\psi}|^2. \quad (25) \]

### 3.3. Analysis of the Ginzburg-Landau equations: Type I and type II Superconductors

The analysis of type I and type II superconductors skizzed in the framework of the London theory will be developed here within the Ginzburg-Landau theory. Let
us consider a uni-dimensional sample in the normal state for $z \to -\infty$ and in the superconducting state for $z \to \infty$. The boundary conditions are

$$\begin{align*}
\psi &= 0, \quad B = H_c \quad \text{pour} \quad z \to -\infty \\
\psi &= \psi_\infty, \quad B = 0 \quad \text{pour} \quad z \to \infty.
\end{align*}$$

(26)

The external field is chosen equal to the critical field $H_c$ such that the system is in thermodynamical equilibrium. With the Gibbs free energy density defined by (2)

$$g(T, H_c) := f(T, B) - \frac{1}{4\pi} B \cdot H_c,$$

we have

$$
\begin{align*}
g(T, H_c) &= g_n(T, 0) - \frac{1}{8\pi} H_c^2 = f_n(T, 0) - \frac{1}{8\pi} H_c^2 \quad z \to -\infty \\
g(T, H_c) &= f_s(T, 0) \quad z \to \infty
\end{align*}
$$

(27)  

(28)

where we used equations (4) and (5)

$$
\begin{align*}
g_n(T, H_c) &= g_n(T, 0) - \frac{1}{8\pi} H_c^2 \\
g_s(T, H_c) &= g_s(T, 0).
\end{align*}
$$

These two limiting values are equal because of the equilibrium condition (6), which prevents one of the phases to develop, at the expense of the other. We introduced in the sample a separation surface between the normal and superconducting states.

In order to understand how a superconductor behaves as a function of the parameters $\xi$ and $\lambda$, it is appropriate to study the energy associated to the surface which separates the normal and the superconducting parts. Let us consider an external field $H_c$ parallel to the separation surface. The energy per unit surface of this system will depend strongly on the values of $\xi$ and $\lambda$, as one can see from the following scheme:
The surface energy is defined by the difference between the Gibbs free energy per unit area and the free energy of a completely normal or superconducting sample [i.e., a sample which satisfies the conditions (28)]

\[ \sigma_{ns} := \int_{-\infty}^{\infty} dz [g - g_s] = \int_{-\infty}^{\infty} dz \left[ f(T, B) - \frac{1}{4\pi} B \cdot H_c - f_s(T, 0) \right]. \] (29)

By introducing the Ginzburg-Landau free energy density (13), we obtain

\[ \sigma_{ns} = \int_{-\infty}^{\infty} dz \left[ f_n(T, 0) + \alpha |\psi|^2 + \beta \frac{1}{2} |\psi|^4 + \frac{1}{2m^*} \left( \frac{\hbar}{i} \nabla - \frac{e^*}{c} A \right) \psi \right]^2 + \frac{1}{8\pi} B^2 - \frac{1}{4\pi} B \cdot H_c - f_s(T, 0) \right]. \] (30)

With \( f_s(T, 0) = f_n(T, 0) - H_c^2/8\pi \), this energy becomes

\[ \sigma_{ns} = \int_{-\infty}^{\infty} dz \left[ \alpha |\psi|^2 + \beta \frac{1}{2} |\psi|^4 + \frac{1}{2m^*} \left( \frac{\hbar}{i} \nabla - \frac{e^*}{c} A \right) \psi \right]^2 + \frac{1}{8\pi} (B - H_c)^2 \right]. \] (31)

From the first Ginzburg-Landau equation (14) multiplied by \( \psi^* \) and integrated by parts we find

\[ \int_{-\infty}^{\infty} dz \left[ \alpha |\psi|^2 + \beta \frac{1}{2} |\psi|^4 + \frac{1}{2m^*} \left( \frac{\hbar}{i} \nabla - \frac{e^*}{c} A \right) \psi \right]^2 = 0. \]

Thus the result

\[ \sigma_{ns} = \int_{-\infty}^{\infty} dz \left[ -\frac{\beta}{2} |\psi|^4 + \frac{1}{8\pi} (B - H_c)^2 \right] \]

which may be expressed in terms of the dimensionless quantities defined in (24), where \( z \) is also dimensionless,

\[ \sigma_{ns} = \frac{H_c^2}{8\pi} 2\lambda \int_{-\infty}^{\infty} dz \left[ -\frac{1}{2} \rho^4 + \left( B - \frac{1}{\sqrt{2}} \right)^2 \right] \]

where we notice \( \rho := \psi/\psi_\infty \). By defining the length

\[ \delta := 2\lambda \int_{-\infty}^{\infty} dz \left[ -\frac{1}{2} \rho^4 + \left( B - \frac{1}{\sqrt{2}} \right)^2 \right] \] (32)

we obtain the surface energy

\[ \sigma_{ns} = \frac{H_c^2}{8\pi} \delta. \]

The continuation of the calculations requires the knowledge of the order parameter \( \rho \). For that, we should be able to solve the Ginzburg-Landau equations. However, an analytical solution of these equations is not known, even in the unidimensional
case. We will therefore consider some particular cases. Before, it is interesting to notice that via the gauge transformation
\[ A' = A + \frac{1}{\kappa} \nabla \chi, \]
\[ \psi' = |\psi| e^{i\chi}, \] (33)

it is possible to rewrite the Ginzburg-Landau equations (25) in a form which depends only on the modulus of $|\psi|$ and on $B$. We then obtain (exercise):
\[ |\psi|^2 B = -\nabla \times (\nabla \times B) + \frac{2}{|\psi|} \nabla |\psi| \times (\nabla \times B). \] (34)

As a particular case, let us consider a uni-dimensional system, in which the field $B$ is chosen parallel to the direction $x$, i.e., $B = B(z)e_x, A = -A(z)e_y$. Thus, the Ginzburg-Landau equations (34) become
\[ \rho - \rho^3 + \frac{1}{\kappa^2} \frac{d^2}{dz^2} \rho - \frac{1}{\rho \frac{d \rho}{dz}} \left( \frac{d B}{d z} \right)^2 = 0 \]
\[ B \rho^2 = \frac{d^2}{dz^2} \rho - 2 \frac{d \rho}{\rho d z} \frac{d B}{d z}. \] (35)

These equations are subject to the boundary conditions
\[ \rho = 0, \quad B = 1/\sqrt{2} \quad \text{pour} \quad z \to -\infty \]
\[ \rho = \rho_0, \quad B = 0 \quad \text{pour} \quad z \to \infty. \] (36)

Let us analyse now the different regimes of $\kappa = \lambda/\xi$:
\[ \kappa \ll 1, \quad \kappa \gg 1, \quad \kappa = \kappa_c. \]

• $\kappa \ll 1$

As long as $\rho$ is finite, one may suppose that $B = 0$ because $\lambda$ is very small in this case. Therefore the equation (35) becomes
\[ \frac{1}{\kappa^2} \frac{d^2}{dz^2} \rho + \rho - \rho^3 = 0. \]

This equation has already been solved in (20) and the solutions are
\[ \rho = 0 \quad B = 1/\sqrt{2} \quad \text{pour} \quad z < 0 \]
\[ \rho = \tanh \left( \frac{\kappa z}{\sqrt{2}} \right) \quad B = 0 \quad \text{pour} \quad z > 0 \] (37)

We deduce the length (32)
\[ \delta = 2\lambda \int_{-\infty}^{\infty} dz \frac{1}{2} \left[ 1 - \tanh^4 \left( \frac{\kappa z}{\sqrt{2}} \right) \right] = \frac{4\sqrt{2}}{3} \xi \]

19
which provides a positive surface energy
\[
\sigma_{ns} = \frac{\sqrt{2}}{6\pi} \xi H_c^2.
\]

• \(\kappa \gg 1\)

In this case, the term \(\frac{1}{\kappa^2} \frac{d^2}{dz^2} \rho\) may be neglected. We then have
\[
\left( \frac{dB}{dz} \right)^2 = \rho^4 (1 - \rho^2).
\]

Because \(B\) decreases when \(z\) increases, we have
\[
\frac{dB}{dz} = -\rho^2 \sqrt{1 - \rho^2}.
\]

On the other hand, the second equation (35) may also be written
\[
B = \frac{d}{dz} \left( \frac{1}{\rho^2} \frac{dB}{dz} \right).
\]

Combined with (38) it becomes
\[
B = -\frac{d}{dz} \sqrt{1 - \rho^2}.
\]

By eliminating \(B\) we obtain the equation
\[
\frac{d^2}{dz^2} \sqrt{1 - \rho^2} = \rho^2 \sqrt{1 - \rho^2},
\]
which, with \(u := \sqrt{1 - \rho^2}, \rho^2 = 1 - u^2\), is written
\[
u'' = (1 - u^2) u
\]
or still, with \(u' := du/dz\)
\[
u'^2 = u^2 - \frac{1}{2} u^4 + c
\]
Because \(u \to 0, u' \to 0\) for \(z \to \infty\), we have \(c = 0\). One ends then at the equation (sign minus because \(u\) decreases)
\[
u' = -u \sqrt{1 - \frac{u^2}{2}}.
\]

With the new variable \(u = \sqrt{1 - \rho^2}\) the integral (32) becomes
\[
\delta = 2\lambda \int_{-\infty}^\infty dz \left[ -2u \left( -\frac{u^2}{2} \right)^{1/2} + \sqrt{2} \right] \frac{du}{dz}.
\]

Integration over \(u\), \(u(0) = 1, u(\infty) = 0\) gives
\[
\delta = 2\lambda \int_0^1 du \left[ 2u \left( 1 - \frac{u^2}{2} \right)^{1/2} - \sqrt{2} \right] = \frac{8}{3} (1 - \sqrt{2}) \lambda.
\]

Notice that the surface energy is negative in this case.
\section*{K \equiv \kappa_c}

We have just seen that the surface energy is positive for \( \kappa \ll 1 \) and negative for \( \kappa \gg 1 \). Which is the value of \( \kappa \) for which the surface energy vanishes? From the formula (32) for the length \( \delta \) we conclude that \( \sigma_{ns} = 0 \) when

\[
\sqrt{2}B = 1 - \rho^2
\]

By taking the derivative, we obtain

\[
\frac{dB}{dz} = -\sqrt{2} \rho \frac{d\rho}{dz}
\]

\[
\frac{d^2B}{dz^2} = -\sqrt{2} \left( \frac{d\rho}{dz} \right)^2 - \sqrt{2} \rho \frac{d^2\rho}{dz^2}.
\]

By returning to the Ginzburg-Landau equations (35), the first equation (39) gives

\[
\rho - \rho^3 + \frac{1}{\kappa^2} \frac{d^2\rho}{dz^2} - \frac{2}{\rho} \left( \frac{d\rho}{dz} \right)^2 = 0
\]

and the second

\[
\rho - \rho^3 + 2 \frac{d^2\rho}{dz^2} - \frac{2}{\rho} \left( \frac{d\rho}{dz} \right)^2 = 0.
\]

There is a unique solution satisfying the conditions \( \rho \to 0 \) for \( z \to -\infty \), \( \rho \to 1 \) for \( z \to \infty \), if \( \kappa = 1/\sqrt{2} \). We find then the Abrikosov classification of the superconductors:

\[
\text{Type I} : \quad \kappa < \frac{1}{\sqrt{2}}, \quad \sigma_{ns} > 0
\]

\[
\text{Type II} : \quad \kappa > \frac{1}{\sqrt{2}}, \quad \sigma_{ns} < 0.
\]

The diagrams below provide an illustration of the behavior of \( \rho \) and \( H_c \) at the surface separating a normal conductor from a superconductor.

It is missing to calculate the critical fields \( H_{c1} \) and \( H_{c2} \), what you will do as an exercise, and to precise the notion of vortex line.

\subsection*{3.4. Flux Quantization: the properties of a vortex line}

The idea of flux quantization had already been put forward by London. However, in the framework of the Ginzburg-Landau theory, the flux quantization follows in a natural way, from the uniformity of the complex function which represents the order parameter. Indeed, we can always separate the order parameter in amplitude and phase

\[
\psi = |\psi|e^{i\chi}.
\]
The current density (16) becomes
\[ \mathbf{j} = \frac{e^* \hbar}{m^*} |\psi|^2 \nabla \chi - \frac{e^*}{m^* c} |\psi|^2 \mathbf{A}, \]
from which we get
\[ \nabla \chi = \frac{m^*}{e^* \hbar} \frac{\mathbf{j}}{|\psi|^2} + \frac{e^*}{\hbar c} \mathbf{A}. \] (41)

We know from the Bitter decoration experiments that there is a superconducting state in which only a weak magnetic field is inside the superconductor, and concentrated on the vortex line. Far from it, the current \( \mathbf{j} = 0 \). Therefore, if we integrate (41) over a closed line \( C \), we get
\[ \oint_C \nabla \chi \cdot d\mathbf{r} = \frac{e^*}{\hbar c} \oint_C \mathbf{A} \cdot d\mathbf{r} = \frac{e^*}{\hbar c} \int_{\Sigma} (\nabla \times \mathbf{A}) \cdot d\mathbf{\hat{r}} \]
\[ = \frac{e^*}{\hbar c} \int_{\Sigma} \mathbf{B} \cdot d\mathbf{\hat{r}} = \frac{e^*}{\hbar c} \phi_c, \] (42)
where we have integrated over a ligne \( C \) enclosing the flux line and used the Stokes theorem. We obtain then a phase change of the order parameter \( \psi \) after going through the path \( C \). As \( \psi \) is a uniform function (i.e., \( \psi \) has the same value after the path \( C \)), the phase can only be a multiple of \( 2\pi \). Therefore, by defining \( \chi = \varphi + \text{const.} \), where \( \varphi \) is the azimuthal angle, we obtain
\[ \oint_C \nabla \chi \cdot d\mathbf{r} = \oint_C \nabla \varphi \cdot d\mathbf{r} = \int_0^{2\pi n} d\varphi = 2\pi n, \quad n \in \mathbb{Z}. \]

By assuming \( e^* = 2e \) we find
\[ \phi_c = \frac{\hbar c}{2e} n = n \phi_0 \]
where $\phi_0 = \hbar c/2e$ is the flux quantum.

It is important to notice that if we integrate close to the axis of the vortex, the flux will be weaker because in this case we should take into account the current $\mathbf{j} \neq 0$:

$$
\frac{e^*}{\hbar} \phi_c = \frac{m^*}{e^*} \frac{1}{\psi^2} \int C \mathbf{j} \cdot d\mathbf{r} + 2\pi n.
$$

The flux tube is called a vortex line or simply a vortex. We may represent it with the help of the scheme in the following page.

![Diagram of vortex line](image)

The qualitative properties of a vortex line may be deduced from the Ginzburg-Landau equations (24) and (25), where one introduces the cylindrical coordinates and one considers a field $\mathbf{B} \parallel \mathbf{e}_z$ i.e., $\nabla \times \mathbf{B} = -(dB/dr)e_\varphi$. Thus, with $\rho = |\psi|$ we have

$$
\frac{1}{\kappa^2 r \frac{d}{dr}} \frac{d}{dr} \frac{d\rho}{dr} - \frac{1}{\rho^3} \left( \frac{dB}{dr} \right)^2 + \rho - \rho^3 = 0
$$

$$
\rho^2 \mathbf{B} = -\nabla(\nabla \cdot \mathbf{B}) + \nabla^2 \mathbf{B} - \frac{2}{\rho} \frac{d\rho}{dr} \mathbf{e}_r \times \frac{dB}{dr} \mathbf{e}_\varphi
$$

$$
= \left( \frac{d}{r dr} \frac{d\rho}{dr} - \frac{2d\rho dB}{\rho dr dr} \right) \mathbf{e}_z.
$$

We obtain then the equation

$$
B = \frac{1}{r} \frac{d}{dr} \frac{r dB}{dr}.
$$
With the boundary conditions $\rho = 1$ and $dB/dr = 0$ for $r \to \infty$ [in fact, for $r \to \infty$ we have $j = 0$ and because $\nabla \times B \sim j$, ...]. In cylindrical coordinates [$d\sigma = e_2 r dr d\varphi$] the flux quantization becomes

$$\kappa \int \mathbf{B} \cdot d\sigma = \kappa 2\pi \int_0^\infty r dr B = 2\pi n,$$

where we have introduced a dimensionless relation, with the help of $\kappa := \sqrt{2} e^* H_c \lambda^2 / \hbar c$. With (44) this relation becomes

$$2\pi \frac{\kappa r dB}{\rho^2 dr} \bigg|_0^\infty = 2\pi n,$$

and we find

$$\frac{dB}{dr} = -\rho^2 \frac{n}{\kappa r} \quad \text{pour} \quad r \to 0.$$

By going to (43), around $r \sim 0$, we have the equation

$$\frac{1}{\kappa^2} \frac{d}{dr} \left( r \frac{d\rho}{dr} \right) - \frac{n^2}{\kappa^2 r^2} \rho + (1 - \rho^2) \rho \sim 0,$$

whose solution behaves as

$$\rho \sim r^n \quad \text{pour} \quad r \to 0.$$

When $r \gg 1$, $\rho \to 1$ and equation (44) becomes

$$\frac{d^2 B}{dr^2} + \frac{1}{r} \frac{dB}{dr} - B = 0$$

whose solution satisfying the boundary conditions is the modified Bessel function $K_0(r)$

$$B(r) \sim K_0(r).$$

In the limit $\kappa \gg 1/\sqrt{2}$ (extreme type II), the spatial variation of $\rho$ is confined to the region $r \ll \kappa^{-1}$ [i.e., $r \leq \xi$ in the conventional unities]. The solution $B(r) \sim K_0(r)$, $dB/dr \sim -K_1(r)$ is also valid for small $r$ because for $\kappa \gg 1/\sqrt{2}$, $\rho$ tends rapidly to 1 in comparison with the slow variation of $B$. Therefore for $r \ll 1$ we have

$$\frac{dB}{dr} \sim -K_1(r) \sim -\frac{1}{r} = -\rho^2 \frac{n}{\kappa r}, \quad \rho = 1.$$

This means that (45) is also valid for $r \ll 1$ and not only for $r \ll \kappa^{-1}$. In this case, the solution has the form

$$\rho(r) = 1 - \frac{1}{2} \left( \frac{n}{\kappa r} \right)^2, \quad n\kappa^{-1} \ll r \ll n.$$